LEVEL (13)

AD A110430

FINAL TECHNICAL SUMMARY REPORT

for the period

1 October 1980 - 30 September 1981

THERMODYNAMICS OF ORGANIC COMPOUNDS

DTIC
SELECTED
FEB 3 1982
H

Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

Research sponsored by:

Air Force Office of Scientific Research (NA)
Department of the Air Force

Contract No. AFOSR-ISSA 81-00013
Project No. 2308/B1

FINAL TECHNICAL SUMMARY REPORT

for the period

1 October 1980 - 30 September 1981

THERMODYNAMICS OF ORGANIC COMPOUNDS

Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

41Ø743

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
AFOSR-TR- 82-0023	AD-A110 430	

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
THERMODYNAMICS OF ORGANIC COMPOUNDS	FINAL 1 Oct 80 - 30 Sept 81
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
N K Smith B E Gammon W D Good	AFOSR-ISSA 81-00013

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
BARTLESVILLE ENERGY TECHNOLOGY CENTER DEPARTMENT OF ENERGY BARTLESVILLE, OK 74005-1398	2308/B1 61102F

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA, BLDG 410 BOLLING AIR FORCE BASE, D C 20332	1981
	13. NUMBER OF PAGES
	21

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

RAMJET FUELS
ENTHALPY OF COMBUSTION
VAPOR PRESSURE
HEAT CAPACITY
ALKYLINDANS
ALKYLNAPHTHALENES
HEPTACYCLOTETRADECANE

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The research effort continues to be focussed on high density/high energy hydrocarbons. In cooperation with researchers at Wright-Patterson Air Force Base, heats of combustion are measured for constituents of current ramjet fuels and for finished fuels; meanwhile, pure hydrocarbons are synthesized for heat-of-combustion measurement whose unusual steric or strain energies may contribute to design of high energy/high density fuels of the future. (over)

DD FORM 1 JAN 73 1473A EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Abstract -- continued

Four pure hydrocarbons were studied during the current reporting period that were selected among the alkylnaphthalenes and indans that may exhibit unusual steric energies. One unusual hydrocarbon, with very high density and a "cage-like" molecular structure, was also studied during this period. This substance is undergoing preliminary testing as an experimental fuel. Synthesis and purification of hydrocarbons for future study are in progress at Oklahoma State University. New equipment and procedures were developed for application of the differential scanning calorimeter on measurements of heat capacity of fuels and their constituents.

Preparation is underway to study the heat of combustion of several special liquid hydrocarbon fuels, in cooperation with researchers at Wright-Patterson Air Force Base.

Results of past and present research done under AFOSR sponsorship were prepared for publication, and two journal articles were published.

FINAL TECHNICAL SUMMARY REPORT

THERMODYNAMICS OF ORGANIC COMPOUNDS

* ☆ * * * * * * * * * *

Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

Project Director: W. D. Good   Report* prepared by:

N. K. Smith
B. E. Gammon
W. D. Good

W. D. Good, Division Director
H. R. Johnson, Director

* Synthesis and purification of research samples were
provided by Professor E. J. Eisenbraun, Oklahoma State
University. Samples were produced by purchase agreement
for this project.

TABLE OF CONTENTS

FOREWORD

This research program consists of an integrated and inter-
related effort of basic and applied research in chemical
thermodynamics and thermochemistry. Knowledge of variation
of physical and thermodynamic properties with molecular
structure is used to select compounds for study that be-
cause of high ring strain or unusual steric effects may
have good energy characteristics per unit volume or per
unit mass and thus be useful in the synthesis of high
energy fuels. These materials are synthesized, and their
thermodynamic properties are evaluated. In cooperation
with researchers at Wright-Patterson Air Force Base,
ramjet fuels currently in use are subjected to careful
thermodynamic evaluation by measurements of heat capacity,
enthalpy of combustion and vapor pressure.

ABSTRACT

The research effort continues to be focused on high
density/high energy hydrocarbons. In cooperation with
researchers at Wright-Patterson Air Force Base, heats of
combustion are measured for constituents of current ramjet
fuels and for finished fuels; meanwhile, pure hydrocarbons
are synthesized for heat-of-combustion measurement whose
unusual steric or strain energies may contribute to design
of high energy/high density fuels of the future.

Four pure hydrocarbons were studied during the current
reporting period that were selected among the alkylnaph-
thalenes and indans that may exhibit unusual steric energies.
One unusual hydrocarbon, with very high density and a "cage-
like" molecular structure, was also studied during this
period. This substance is undergoing preliminary testing as
an experimental fuel. Synthesis and purification of hydro-
carbons for future study are in progress at Oklahoma State
University. New equipment and procedures were developed for
application of the differential scanning calorimeter on
measurements of heat capacity of fuels and their constitu-
ents.

Preparation is underway to study the heat of combustion of
several special liquid hydrocarbon fuels in cooperation with
researchers at Wright-Patterson Air Force Base.

Results of past and present research done under AFOSR
sponsorship were prepared for publication, and two journal
articles were published.

RESEARCH PROGRESS

1. ENTHALPY OF COMBUSTION

    a. Alkylnaphthalenes and Indans

    Enthalpies of combustion were measured for four
    compounds. Summaries of combustion experiments,
    pictorial formulas, combustion reactions, and
    molar values of enthalpy of combustion and forma-
    tion are given for 1-ethyl-8-methylnaphthalene
    (Tables 1 and 2), 1-isopropyl-8-methylnaphthalene
    (Tables 3 and 4), and 1,6-dimethylindan (Tables 7
    and 8). Similar measurements have been reported
    for 2-ethyl-6-methylnaphthalene,[1] a series of di-
    methylnaphthalenes,[2] and 1,7-dimethylindan.[3]

    Synthesis of 2-isopropyl-6-methylnaphthalene and
    1-isopropyl-7-methylindan are in progress in the
    laboratories of Professor E. J. Eisenbraun at
    Oklahoma State University. It is not yet possible
    to make all of the gaseous state comparisons de-
    sirable, but qualitatively it can be said that the
    1,8-substituted naphthalenes are showing the ex-
    pected high steric energies and tnat the 1,7-substi-
    tuted indans are showing little or no steric effect.
    This may yet be found with more alkyl group substi-
    tution in the 1- position.

---

[1] AFOSR Final Technical Summary Report, 1976-1977.
[2] W. D. Good, *J. Chem. Thermodynamics*, 5, 715 (1973).
[3] AFOSR Final Technical Summary Report, 1979-1980.

TABLE 1. Summary of Calorimetric Experiments with 1-Ethyl-8-methylnaphthalene[a]

$(\text{cal}_{th} = 4.184 \text{ J})$

	1	2	3	4	5	6	7	8	9
m'(compound))/g	0.729397	0.731212	0.741948	0.752954	0.742284	0.743978	0.743330	0.744720	0.744702
m''(auxiliary oil)/g	0.067386	0.063239	0.053567	0.043203	0.053257	0.051743	0.052305	0.050792	0.050786
m'''(fuse)/g	0.001003	0.000980	0.000936	0.000959	0.000959	0.000918	0.000963	0.001001	0.000895
$n'(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_r - t_i + \Delta t_{corr})/K$	2.00793	2.00084	2.00059	2.00024	2.00075	2.00132	2.00100	2.00022	1.99971
$\varepsilon(\text{calor})(-\Delta t_c)/\text{cal}_{th}$	-8046.27	-8017.85	-8016.86	-8015.43	-8017.50	-8019.80	-8018.50	-8015.36	-8013.34
$\varepsilon(\text{cont})(-\Delta t_c)/\text{cal}_{th}$ [b]	-8.94	-8.74	-8.82	-8.68	-8.82	-8.87	-8.75	-8.76	-8.83
$\Delta E_{ign}/\text{cal}_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
$\Delta E(\text{corr to std states})/\text{cal}_{th}$ [c]	3.95	3.94	3.97	3.99	3.97	3.97	3.97	3.97	3.97
$(-m''(\Delta E_c^\circ/m)(\text{auxiliary oil}))/\text{cal}_{th}$	741.55	695.91	588.81	475.42	586.06	569.40	575.59	558.93	558.87
$(-m'''(\Delta E_c^\circ/m)(\text{fuse}))/\text{cal}_{th}$	4.06	3.97	3.79	3.88	3.88	3.72	3.90	4.05	3.62
$(m'(\Delta E_c^\circ/m)(\text{compound}))/\text{cal}_{th}$	-7305.47	-7322.58	-7428.93	-7540.83	-7432.24	-7451.39	-7443.62	-7456.99	-7455.53
$[(\Delta E_c^\circ/m)(\text{compound})]/\text{cal}_{th}$ per g	-10015.77	-10014.31	-10012.74	-10015.00	-10012.66	-10015.60	-10013.88	-10013.14	-10011.43
$[(\Delta E_c^\circ/m)(\text{compound})]/\text{cal}_{th}$ per g	-10013.84 ± 0.49 (mean and standard deviation of the mean)								

[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al. Experimental Thermochemistry, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

[b] $\varepsilon^i(\text{cont})(t_i - 298.15 \text{ K}) + \varepsilon^f(\text{cont})(298.15 \text{ K} - t_f + \Delta t_{corr})$.

[c] Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

2

TABLE 2. Derived Molar Thermochemical Values for
1-Ethyl-8-methylnaphthalene at 298.15 K

$(cal_{th} = 4.184 J)$

$$C_{13}H_{14}(l) + 33/2 \ O_2(g) = 13 \ CO_2(g) + 7 \ H_2O(l)$$
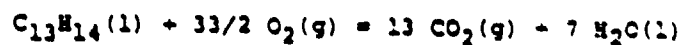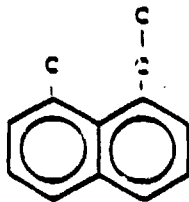
$\Delta Ec°/M$ =	-10015.77 CAL G^{-1}
	-10014.31
	-10012.74
	-10015.00
	-10012.66
	-10015.60
	-10013.88
	-10013.14
	-10011.43
MEAN	-10013.84
STD. DEV. OF MEAN	±0.49

$\Delta Ec°$ =	-1704.92 ± 0.26 KCAL MOL^{-1}
$\Delta Hc°$ =	-1707.00 ± 0.26 KCAL MOL^{-1}
$\Delta Hf°$ =	+6.13 ± 0.30 KCAL MOL^{-1}
$\Delta Hf°(g)$ =	+23.45 ± 0.35 KCAL MOL^{-1}
CO_2 RECOVERY	99.991 ± 0.005% (MEAN AND SDM)

3

TABLE 3. Summary of Calorimetric Experiments with 1-Isopropyl-8-methylnaphthalene[a]

(cal_{th} = 4.184 J)

|	1	2	3	4	5	6	7	8
m'(compound)/g	0.688767	0.703508	0.708868	0.704550	0.729591	0.716324	0.724230	0.690375
m''(auxiliary oil)/g	0.096079	0.083049	0.078671	0.082190	0.059492	0.071274	0.063638	0.095237
m'''(fuse)/g	0.000963	0.000918	0.000868	0.000920	0.001033	0.001053	0.001173	0.001008
n^i(H_2O)/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
Δt_c/K = $(t_f - t_i + \Delta t_{corr})$/K	1.99968	2.00115	2.00205	2.00142	2.00219	2.00119	2.00037	2.00164
ε(calor)$(-\Delta t_c)$/cal_{th}	-8013.69	-8019.56	-8023.17	-8020.65	-8023.75	-8019.72	-8016.43	-8021.51
ε(cont)$(-\Delta t_c)$/cal_{th}[b]	-8.71	-8.70	-8.69	-8.75	-8.74	-8.70	-8.68	-8.71
ΔE_{ign}/cal_{th}	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
ΔE(corr to std states)/cal_{th}[c]	3.75	3.78	3.79	3.78	3.83	3.80	3.81	3.75
$(-m''(\Delta E_c^\circ/m)$ (auxiliary oil))/cal_{th}	1057.29	913.90	865.73	904.45	654.67	784.33	700.30	1048.22
$(-m'''(\Delta E_c^\circ/m)$ (fuse))/cal_{th}	3.90	3.72	3.51	3.72	4.18	4.26	4.75	4.08
$(m'(\Delta E_c^\circ/m)$ (compound))/cal_{th}	-6957.29	-7106.67	-7158.65	-7117.26	-7369.63	-7235.84	-7316.07	-6974.19
$((\Delta E_c^\circ/m)$ (compound))/cal_{th} per g	-10101.08	-10101.76	-10101.56	-10101.86	-10101.04	-10101.36	-10101.86	-10102.02
$((\Delta E_c^\circ/m)$ (compound))/cal_{th} per g	-10101.57 ± 0.13 (mean and standard deviation of the mean)							

a The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience; 1956.

b ε^i(cont)$(t_i - 298.15$ K) + ε^f(cont)$(298.15$ K - $t_f + \Delta t_{corr})$.

c Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 4.   Derived Molar Thermochemical Values for
1-Isopropyl-8-methylnaphthalene at 298.15 K

$(cal_{th} = 4.184\ J)$

$$C_{14}H_{16}(l) + 18\ O_2(g) = 14\ CO_2(g) + 8\ H_2O(l)$$
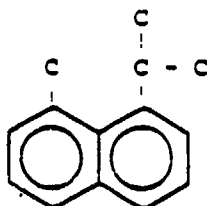
$$\Delta E c^{\circ}/M = -10101.08\ CAL\ G^{-1}$$

$$-10101.76$$

$$-10101.56$$

$$-10101.86$$

$$-10101.04$$

$$-10101.36$$

$$-10101.86$$

$$-10102.02$$

MEAN -10101.57

STD. DEV. OF MEAN ± 0.13

$$\Delta E c^{\circ} = -1861.55 \pm 0.24\ KCAL\ MOL^{-1}$$

$$\Delta H c^{\circ} = -1863.92 \pm 0.24\ KCAL\ MOL^{-1}$$

$$\Delta H f^{\circ} = +0.69 \pm 0.30\ KCAL\ MOL^{-1}$$

CO$_2$ RECOVERY   99.96 $\pm$ 0.01% (MEAN AND SDM)

5

TABLE 5. Summary of Calorimetric Experiments with 1-Isopropyl-6-methylindan[a]

$$(\mathrm{cal_{th}} = 4.184\ J)$$

|	1	2	3	4	5	6
m'(compound)/g	0.703833	0.709730	0.698597	0.747474	0.754828	0.742998
m''(auxiliary oil)/g	0.063037	0.056848	0.070093	0.036883	0.026612	0.029290
m'''(fuse)/g	0.001245	0.001006	0.001271	0.001196	0.001036	0.001101
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	1.99461	1.99280	2.00063	2.03585	2.02654	2.00320
ε(calor)$(-\Delta t_c)/\mathrm{cal_{th}}$	-7993.36	-7986.10	-8017.49	-8158.64	-8121.30	-8027.78
ε(cont)$(-\Delta t_c)/\mathrm{cal_{th}}$[b]	-8.69	-8.69	-8.66	-9.67	-9.60	-9.49
$\Delta E_{ign}/\mathrm{cal_{th}}$	0.18	0.18	0.18	0.18	0.18	0.18
ΔE(corr to std states)$/\mathrm{cal_{th}}$[c]	3.38	3.38	3.38	3.50	3.50	3.40
$[-m''(\Delta E_c^\circ/m)$(auxiliary oil)$]/\mathrm{cal_{th}}$	693.68	625.57	771.33	405.87	292.85	322.32
$[-m'''(\Delta E_c^\circ/m)$(fuse)$]/\mathrm{cal_{th}}$	5.04	4.07	5.15	4.84	4.19	4.45
$[m'(\Delta E_c^\circ/m)$(compound)$]/\mathrm{cal_{th}}$	-7299.76	-7361.56	-7246.12	-7753.92	-7830.18	-7706.87
$[(\Delta E_c^\circ/m)$(compound)$]/\mathrm{cal_{th}}$ per g	-10371.44	-10372.34	-10372.39	-10373.50	-10373.46	-10372.66
$[(\Delta E_c^\circ/m)$(compound)$]/\mathrm{cal_{th}}$ per g	-10372.63 ± 0.32 (mean and standard deviation of the mean)					

a The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

b ε^i(cont)$(t_i - 298.15\ K) + \varepsilon^f$(cont)$(298.15\ K - t_f + \Delta t_{corr})$.

c Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

6

TABLE 6. Derived Molar Thermochemical Values for
1-Isopropyl-6-methylindan at 298.15 K

$(\text{cal}_{th} = 4.184\ J)$

$$C_{13}H_{18}(l) + 35/2\ O_2(g) = 13\ CO_2(g) + 9\ H_2O(l)$$
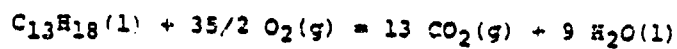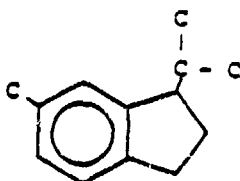
$\Delta Ec^\circ/M = -10371.44\ \text{CAL}\ G^{-1}$

-10372.34

-10372.39

-10373.50

-10373.46

-10372.66

MEAN -10372.63

STD. DEV. OF MEAN ± 0.32

$\Delta Ec^\circ = -1807.83 \pm 0.26\ \text{KCAL MOL}^{-1}$

$\Delta Hc^\circ = -1810.50 \pm 0.26\ \text{KCAL MOL}^{-1}$

$\Delta Hf^\circ = -27.00 \pm 0.30\ \text{KCAL MOL}^{-1}$

CO$_2$ RECOVERY $99.98 \pm 0.03\%$ (MEAN AND SDM)

7

TABLE 7. Summary of Calorimetric Experiments with 1,6-Dimethylindan[a]

(cal_th = 4.184 J)

	1	2	3	4	5	6	7	8
m'(compound)/g	0.703631	0.712170	0.718148	0.732350	0.711815	0.714155	0.701059	0.691078
m''(auxiliary oil)/g	0.072266	0.065313	0.060040	0.047014	0.066093	0.063630	0.076300	0.080669
m'''(fuse)/g	0.001150	0.000970	0.001068	0.001201	0.000880	0.000972	0.000936	0.001006
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	1.99688	1.99940	2.00004	2.00129	2.00030	1.99987	2.00127	1.98779
ε(calor)$(-\Delta t_c)$/cal$_{th}$	-8001.99	-8012.08	-8014.66	-8019.65	-8015.71	-8013.98	-8019.56	-7965.56
ε(cont)$(-\Delta t_c)$/cal$_{th}$[b]	-8.82	-8.69	-8.88	-8.81	-8.86	-8.89	-8.83	-8.72
ΔE_{ign}/cal$_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
ΔE(corr to std states)/cal$_{th}$[c]	3.56	3.58	3.59	3.61	3.58	3.58	3.56	3.52
$[-m''(\Delta E^\circ_c/m)$(auxiliary oil)]/cal$_{th}$	795.24	718.74	660.71	517.36	727.32	700.21	839.64	887.71
$[-m'''(\Delta E^\circ_c/m)$(fuse)]/cal$_{th}$	4.66	3.93	4.32	4.86	3.56	3.94	3.79	4.97
$[m'(\Delta E^\circ_c/m)$(compound)]/cal$_{th}$	-7207.17	-7294.35	-7354.74	-7502.45	-7289.93	-7314.96	-7181.23	-7078.79
$[(\Delta E^\circ_c/m)$(compound)]/cal$_{th}$ per g	-10242.83	-10242.42	-10241.26	-10244.35	-10241.33	-10242.82	-10243.40	-10243.11
$[(\Delta E^\circ_c/m)$(compound)]/cal$_{th}$ per g	-10242.69 ± 0.36 (mean and standard deviation of the mean)							

a The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.
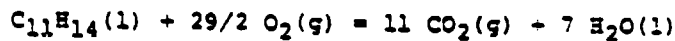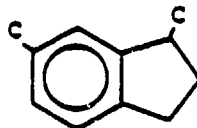
b ε^i(cont)$(t_i - 298.15 K) + \varepsilon^f$(cont)$(298.15 K - t_f + \Delta t_{corr})$.

c Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

8

TABLE 8. Derived Molar Thermochemical Values for
1,6-Dimethylindan at 298.15 K

$(cal_{th} = 4.184$ J$)$

$$C_{11}H_{14}(l) + 29/2\ O_2(g) = 11\ CO_2(g) + 7\ H_2O(l)$$

$$\Delta Ec^\circ/M = -10242.83 \text{ CAL G}^{-1}$$

$$-10242.42$$
$$-10241.26$$
$$-10244.35$$
$$-10241.33$$
$$-10242.82$$
$$-10243.40$$
$$-10243.11$$

MEAN -10242.69

STD. DEV. OF MEAN ± 0.36

$$\Delta Ec^\circ = -1497.83 \pm 0.20 \text{ KCAL MOL}^{-1}$$

$$\Delta Hc^\circ = -1499.91 \pm 0.20 \text{ KCAL MOL}^{-1}$$

$$\Delta Hf^\circ = -12.86 \pm 0.25 \text{ KCAL MOL}^{-1}$$

CO_2 RECOVERY $99.96 \pm 0.01\%$ (MEAN AND SDM)

b. High Density/High Energy Hydrocarbons

An unusual hydrocarbon with cage-like molecular struc-
ture, heptacyclotetradecane, was prepared and purified
in the laboratories of Professor Alan Marchand at the
University of Oklahoma. This crystalline material
of high density should have excellent characteristics
as a solid fuel or in slurry or solution applications.
Summaries of its combustion experiments, its pictorial
formula, the combustion reaction, and molar values of
enthalpy of combustion and formation are given in
Tables 9 and 10.

TABLE 9. Summary of Calorimetric Experiments with Heptacyclotetradecane[a]

$(\text{cal}_{th} = 4.184 \text{ J})$

|	1	2	3	4	5	6	7	8
m'(compound)/g	0.754177	0.797711	0.795936	0.800069	0.802865	0.803835	0.800235	0.801337
m'''(fuse)/g	0.001743	0.001925	0.001883	0.001811	0.001593	0.001935	0.001811	0.001964
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	1.88629	1.9 537	1.99098	2.00102	2.00785	2.01057	2.00139	2.00442
$\varepsilon(\text{calor})(-\Delta t_c)/\text{cal}_{th}$	-7559.28	-7996.39	-7978.82	-8019.04	-8046.41	-8057.32	-8020.54	-8032.68
$\varepsilon(\text{cont})(-\Delta t_c)/\text{cal}_{th}$[b]	-8.11	-8.63	-8.61	-8.65	-8.68	-8.74	-8.68	-8.69
$\Delta E_{ign}/\text{cal}_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
$\Delta E_{(\text{corr to std states})}/\text{cal}_{th}$[c]	3.73	3.98	3.97	4.00	4.01	4.02	4.00	4.00
$[-m'''(\Delta E^\circ_c/m)(\text{fuse})]/\text{cal}_{th}$	7.06	7.80	7.63	7.34	6.45	7.84	7.34	7.96
$[m'(\Delta E^\circ_c/m)(\text{compound})]/\text{cal}_{th}$	-7556.42	-7993.07	-7975.65	-8016.17	-8044.45	-8054.03	-8017.71	-8029.23
$((\Delta E^\circ_c/m)(\text{compound}))/\text{cal}_{th}$ per g	-10019.42	-10020.00	-10020.47	-10019.35	-10019.68	-10019.50	-10019.2.	-10019.79
$((\Delta E^\circ_c/m)(\text{compound}))/\text{cal}_{th}$ per g	-10019.68 ± 0.14 (mean and standard deviation of the mean)							

a   The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

b $\varepsilon^i(\text{cont})(t_i - 298.15 \text{ K}) + \varepsilon^f(\text{cont})(298.15 \text{ K} - t_f + \Delta t_{corr})$.

c   Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

11

TABLE 10. Derived Molar Thermochemical Values for
Heptacyclotetradecane at 298.15 K

$(cal_{th} = 4.184$ J$)$

$$C_{14}H_{16}(c) + 18 \ O_2(g) = 14 \ CO_2(g) + 8 \ H_2O(1)$$
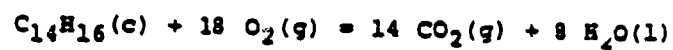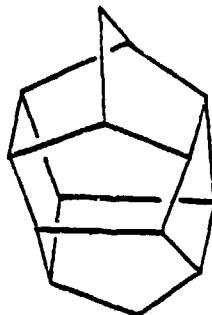
$\Delta E_c^\circ/M$ =	-10019.42 CAL/G
	-10020.00
	-10020.47
	-10019.35
	-10019.68
	-10019.50
	-10019.20
	-10019.79
MEAN	-10019.68 CAL/G
STD. DEV. OF MEAN	±0.15 CAL/G
ΔE_c° =	-1846.46 ± 0.24 KCAL/MOL
ΔH_c° =	-1848.83 ± 0.24 KCAL/MOL
ΔH_f° =	-14.40 ± 0.30 KCAL/MOL
CO_2 RECOVERY	(99.90 ± 0.01)% (MEAN AND SDM)

12

2. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Measurements were not made on materials for this project during the past year; however, new equipment and procedures were developed for applications of the DSC to measurements on such materials. The commercial cells used for DSC have three severe limitations: (1) they cannot be filled to more than 15%, usually less, of the volume available for the sample; (2) they cannot withstand more than 2 atmospheres of internal pressure; and (3) they do not make good thermal contact with the DSC head during measurements. For these reasons, reusable screw-cap cells were designed and built to obviate these problems. These cells were used to determine results reported last year on JP-10 and RJ-6. The cells still had one deficiency which has been eliminated by a new design. In the previous version, a sheet gasket was required for sealing the cells. Upon sealing the sheet gasket was extruded to form a wrinkle into the interior volume of the cell; this led to an uncertainty in the volume available to the sample. Equation 1 shows how the observed heat capacity, c_v^{II}, along the saturation line designated by σ, depends on the total volume, V^τ, available to the total number of moles of the sample, n^τ, of a pure substance.

$$nc_v^{II} = n^\ell c_\sigma^\ell + n^g c_\sigma^g - T\gamma_\sigma \left(\frac{n^\ell}{\rho^\ell}\ \alpha_\sigma^\ell + \frac{n^g}{\rho^g}\ \alpha_\sigma^g \right)$$

$$c_v^{II} = \left(c_\sigma^\ell - T\gamma_\sigma \alpha_\sigma^\ell / \rho^\ell \right) + \left(\frac{V^\tau}{n^\tau} - \frac{1}{\rho^\ell} \right) T \left(\frac{d^2\rho}{dT^2} \right)_\sigma$$

$$c_p^\ell = c_\sigma^\ell + T\alpha_p^\ell\ \gamma_\sigma / \rho^\ell \tag{1}$$

$$\gamma_\sigma = \left(\frac{d\rho}{dT} \right)_\sigma$$

$$\alpha_\sigma = -\left(\frac{d\ell n(\rho^\ell)}{dT} \right)_\sigma$$

If the vapor pressure is small, the volume dependence is not significant, but for pressures even near or above boiling, this term can be a significant fraction of the measured value. For this reason, the cells were redesigned with a cone-shaped seal so that only a ring gasket was required for sealing, and thereby the internal volume of the sealed cells can be determined by a simple measurement with a micrometer. Thus, appropriate corrections can be determined and made with measurements from these cells.

4.   PUBLICATIONS

Thermodynamic Properties of Cyclopropylamine, Cyclpentyl-amine and Methylenecyclobutane by H. L. Finke, J. F. Messerly and S. H. Lee-Bechtold. *Journal of Chemical Thermodynamics*, 13, No. 4, 345-355 (1981).

Vapor Heat Capacity and Enthalpy of Vaporization of Six Miscel-laneous Organic Compounds by I. A. Hossenlopp and D. W. Scott. *Journal of Chemical Thermodynamics*, 13, No. 5, 405-414 (1981).

DISTRIBUTION LIST

CONTRACTORS

Aerospace Corporation
The Iv n L Getting Laboratories
Attn: Dr Charles M Randall
P O Box 95085
Los Angeles, CA 90045

CINDAS
Purdue University Research Park
Attn: Dr H H Li
2595 Yeager Road
West Lafayette, IN 47907

Department of Energy
Bartlesville Energy Technology
  Center
Attn: Mr William D Good
Bartlesville, OK 74003

Dow Chemical Company
Thermal Laboratory, Bldg 1707
Attn: Dr Malcolm Chase
Midland, MI 48640

University of Manchester/UMIST
Department of Metallurgy
Attn: Dr Roy Taylor
Grosvenor Street
Manchester M1 7HS, ENGLAND

Department of Energy
Pittsburgh Energy Technology
  Center
Attn: Dr Francis E Spencer, Jr
P. O. Box 10940
Pittsburgh, PA 15236

National Bureau of Standards
Thermophysics Division
Attn: Dr Ared Cezairliyan
Washington, DC 20234

National Bureau of Standards
Chemical Thermodynamics Division
Attn: Dr Stan Abramowitz
       Mr David Ditmars
Washington, DC 20234

University of Nevada
Mackay School of Mines
Attn: Prof Eugene Miller
Reno, NV 89507

Purdue University
School of Mechanical Engineering
Properties Research Laboratory
Attn: Dr R F Taylor
2595 Yeager Road
West Lafayette, IN 47907

Space Sciences, Inc
Attn: Mr Milton Farber
135 W Maple
Monrovia, CA 91016

SRI International
Physical Sciences Division
Attn: Dr D L Hildenbrand
Menlo Park, CA 94025

NON-CONTRACTORS

AFML/MXE (L Scott Theibert)
Wright-Patterson AFB, OH 45433

AFML/LP (Dr Merrill L Minges)
Wright-Patterson AFB, OH 45433

AFML/MBC (Dr W C Kessler)
Wright-Patterson AFB, OH 45433

Jet Propulsion Laboratory
Attn: Mr. Theodore W Price
4800 Oak Grove Drive
Pasadena, CA 91103

Johns Hopkins University
Applied Physics Laboratory
Attn: Dr Robert Fristrom
Johns Hopkins Road
Laurel, MD 20810

NON-CONTRACTORS--Continued

AFRPL/LKCB (Mr Curtis C Selph)
Edwards AFB, CA 93523

AFRPL/PACP (Dr David Mann)
Edwards AFB, CA 93523

AFWL/ALD (Dr Leroy Wilson)
Kirtland AFB, NM 87117

AFWL/ALD (Major David S Olson)
Kirtland AFB, NM 87117

AFAOL/RJT (Dr F D Stull)
Wright-Patterson AFB, OH 45433

U.S. Army Research Office
Attn: Dr David R Squire
P O Box 12211
Research Triangle Park, NC 27709

Atlantic Research Corporation
Attn: Dr Charles Henderson
5390 Cherokee Avenue
Alexandria, VA 22314

University of California
Department of Chemistry
Attn: Dr Leo Brewer
Berkeley, CA 94700

Cornell University
Department of Chemistry
Attn: Dr S H Bauer
Ithica, NY 14850

NSSC
Department of the Navy
Code NSEA-0331
Attn: Mr John W Murrin
Washington, DC 20360

Naval Ordnance Station
Attn: Mr Al Camp
Indian Head, MD 20640

NASA
Lewis Laboratories (Mail Stop 6-1)
Attn: Mr Sanford Gordon
Cleveland, OH 44135

NAS-NRC
Numerical Data Advisory Board
2101 Constitution Avenue, NW
Washington, DC 20418

National Bureau of Standards
OSRD
Attn: Dr David Lide
Washington, DC 20234

National Bureau of Standards
Chemical Thermodynamics Division
Attn: Mr Donald D Wagman
Washington, DC 20234

National Bureau of Standards
Office of Standard Reference
  Materials
Attn: Dr Richard Kirby
Washington, DC 20234

National Bureau of Standards
Thermophysical Properties Division
Attn: Dr Jerry Hust
Boulder, CO 80302

Office of Naval Research
Attn: Mr Rudolph Marcus
1030 E Green Street
Pasadena, CA 91101

Office of Naval Research
Power Program, Code 473
Attn: Dr Richard Miller
800 North Quincy Street
Arlington, VA 22217

Rice University
Department of Chemistry
Attn: Dr John Margrave
Houston, TX 77001

United Technologies Corporation
Chemical Systems Division
Attn: Dr R O MacLaren
Sunnyvale, CA 94086

Chemical Propulsion Information
  Agency
APL/JHU (2 copies)
Johns Hopkins Road
Laurel, MD 20810